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DISCUSSION MEETING ON  
THERMODYNAMICS OF ALLOYS

May 23-26, 1990  
SANT FELIU DE GUIXOLS, SPAIN

ABSTRACTS

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**DISCUSSION MEETING ON  
THERMODYNAMICS OF ALLOYS**

**May 23-26, 1990  
SANT FELIU DE GUIXOLS, SPAIN**

**ABSTRACTS**

## LOCAL ORGANIZING COMMITTEE

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M.D. Baró, S. Bordas y S. Suriñach  
*Grupo de Física de Materiales.*  
*Universidad Autónoma de Barcelona.*  
*Bellaterra (Barcelona).*

N. Clavaguera  
*Departamento de Estructura y Constituyentes de la Materia.*  
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**Wednesday, May 23**

8.30 Registration  
9.00 Opening Remarks  
9.05 PL A: *H.F. Franzen*, USA  
10.05 A1: *H. Ipser*, Austria  
10.25 A2: *R. Lück*, Germany  
10.45 Coffee Break (Posters can be placed)  
  
11.10 A3: *Th. Hehenkamp*, Germany  
11.30 A4: *F. Faupel*, Germany  
11.50 A5: *V. Torra*, Spain  
12.10 GENERAL DISCUSSION  
13.20 Lunch Break  
  
16.30 PL B: *H. Brodowsky*, Germany  
17.30 B1: *A. Mikula*, Austria  
17.50 B2: *J.C. Gachon*, France  
18.10 Coffee Break + Posters  
  
18.30 B3: *W. Sitte*, Austria  
18.40 B4: *R. Baret*, France  
19.00 B5: *Ch.B. Alcock*, USA  
19.20 GENERAL DISCUSSION

**Thursday, May 24**

9.00 PL C: *B. Sundman*, Sweden  
10.00 C1: *A.V.Ljakutkin*, SSR (Withdrawn)  
10.20 Coffee Break + Posters  
  
10.40 C2: *A.M. Azad*, India  
11.00 C3: *M. Baricco*, Italia  
11.20 C4: *M.T. Clavaguera-Mora*, Spain  
11.40 GENERAL DISCUSSION  
12.40 Lunch Break  
  
14.30 Excursion departure to Girona. The tour will conclude with a dinner in a typical restaurant.

**Friday, May 25**

9.00 PL D: *G. Inden*, Germany  
10.00 D1: *A. Hellawell*, USA  
10.20 D2: *C. Colinet*, France  
10.40 Coffee Break + Posters  
  
11.00 D3: *T. Tanaka*, Japan  
11.20 D4: *D. Quitmann*, Germany  
11.40 D5: *G. Borzone*, Italia  
12.00 GENERAL DISCUSSION  
13.00 Lunch Break  
  
16.30 PL E: *J. Hertz*, France  
17.30 E1: *J.E. Morral*, USA  
17.50 Coffee Break + Posters  
  
18.10 E2: *W. Lengauer*, Austria  
18.30 E3: *F. Sommer*, Germany  
18.50 E4: *Z. Moser*, Poland  
19.10 DISCUSSION

**Saturday, May 26**

9.00 PL F: *M.-L. Saboungi*, USA  
10.00 F1: *O.J. Kleppa*, USA  
10.20 Coffee Break + Posters  
  
10.40 F2: *D. Quitmann*, Germany  
11.00 F3: *R. Yavari*, France  
11.20 F4: *R. Castanet*, France  
11.40 GENERAL DISCUSSION  
12.40 Closing Remarks  
13.00 Lunch  
  
15.00 Departure of special coach to Barcelona

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C.B. Alcock

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A.M. Azad, O.M. Sreedharan and J.B. Gnanasmoorthy

*Glass forming ability in chalcogen rich Se-Te-Ge glasses*  
Y. Calventus, M.D. Baró, S. Suriñach, S. Bordas, M.T. Clavaguera-Mora and N. Clavaguera

*Thermodynamic Study of Au-Pb-Pd Ternary Alloys by E.M.F. Measurements*  
S. Spas, J. Riou, J.M. Miane, R. Baret and J.P. Bros

*Thermodynamics of the Cu-Ti and GaMgZn Systems and Metastable Phase formation*  
M. Baricco and L. Battezzati

*Structural and Thermodynamic Properties of Liquid Alloys at the Eutectic Composition: Case of the Gold-Silicon and Germanium-Tellurium Systems*  
C. Bergman, C. Bichara, R. Bellisent, R. Ceolin and P. Chieux

*Monte Carlo simulation of covalent liquids using a quantum mechanical description of the energy*  
C. Bichara, A. Pellegatti, J.-P. Gaspard

*Rare-Earth-Aluminium Alloys: Optimization of Thermodynamic Properties and Phase Diagrams of the La-Al And Ce-Al Systems*  
G. Cacciamani, G. Borzone and R. Ferro

*Gibbs Energy Determination by Chemical Equilibria*  
H. Brodowsky

*Short-Range Order-Disorder Transition in Liquid Alloys According to the Associated Model*  
R. Castanet

*Thermodynamic criteria of glass formation in the As-Sb-Se System*  
M.T. Clavaguera-Mora, S. Suriñach, M.D. Baró and N. Clavaguera

*A Tight-Binding Analysis of the Cohesive Properties in Transition Metal Carbides*  
D.H. Le, C. Colinet and A. Pasturel

*Oxygen partial pressure of Y-Ba-Cu-O From Direct Measurements*  
E. Faupel and Th. Hehenkamp

*Solid State Thermodynamics: Knudsen Cell Mass Spectrometry and High-Temperature X-Ray Diffraction*  
H.F. Franzen

*Experimental Enthalpies of Formation of Some Solid Phases in the Systems PtTi and PtZr*  
N. Selhaoui and J.C. Gachon

*Relative Solid Solubility in Binary Alloys of Transition Metals*  
J.A. Somoza, J.A. Alonso and L.J. Gallego

*The Influence of Crystalline Orientation of Cu-Zn-Al Shape Memory Single Crystals in Thermal Efficiency*  
J.M. Guilemany and E.J. Gil

*Phase Equilibria in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  Superconductors*  
Th. Hehenkamp and F. Faupel

*Three Dimensional Computer Graphics for the Representation of Phase Equilibria in the Quaternary System  $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$*   
J.D. DeLa'O and A. Hellawell

*Determination of the Thermodynamic Properties of Formation of Alloys at High Temperatures*  
J. Hertz

*CVM and its applications to the thermodynamics of alloys*  
G. Inden

*Thermodynamics of Pd-As Alloys*  
H. Ipser, R. Krachler and K.L. Komarek

*Solute-Solvent Drop Calorimetry of Transition Metal Intermetallic Compounds*  
O.J. Kleppa and L. Topor

*Application of the Wagner-Schottky Model to Nonstoichiometric Intermetallic Phases*  
R. Krachler and H. Ipser

*Establishing Phase Relationships by Means of the Temperature Gradient Diffusion Technique*  
W. Lengauer and Peter Ettmayer

*The Metastable Phase in Fe-C Alloys*  
A.V. Liakutkin

*Simple Forms of the Gibbs-Duhem Integration for k-gaseous Multicomponent Systems*  
Z.-C. Wang, R. Lück and B. Predel

*Enthalpy of formation and phase diagram of the Ga-Pb system*  
J.M. Miane, P. Rebouillon, R. Baret, M. Gambino, J.P. Bros

*Thermodynamic Properties of the Ag-Sb-Zn System*  
A. Mikula

*Applications of Solution Models to Diffusivity Studies in Multicomponent Alloys*  
J.E. Morral and Yoon-Ho Son

*Calorimetric Studies on Liquid Al-Li-Mg Alloys*  
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*Long Range Order Parameters for Multicomponent Compounds*  
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*Some Relations Between the Enthalpy of Mixing and Deviations From Free Electron Behaviour Observed in Liquid Ternary Cu-Ag-Ge Alloys*  
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*Thermodynamic Effects, Seen on the Atomic Sites, in Strongly Bound Liquid Alloys*

K. Ott, B. Balschun, M. Dürrwächter, M.A. Haghani, M.v. Hartrott and D. Quitmann

*Liquid alloys with strong interactions*

M.-L. Saboungi

*Thermodynamic Investigation of the System Ag-Nb-Te*

A. Brunner, H.P. Fritzer and W. Sitte

*Enthalpy of Formation of Ni<sub>3</sub>Al with Ternary Additions*

F. Sommer, S. Kek and K. Rzyman

*Review of Alloys Modelling*

B. Sundman

*A Solution Model for the Relation Between Enthalpy of Mixing and Excess Entropy in Liquid Binary Alloys*

T. Tanaka, N.A. Gokcen, Z. Morita and P.J. Spencer

*New and Old Tools in Martensitic Transformation Studies*

A. Amengual, V. Torra, A. Isalgué and F. Marco

*Disorder-Order Transition Kinetics in L1<sub>2</sub> type Alloys*

R. Yavari, M.D. Baró, S. Suriñach and R.W. Cahn

# ABSTRACTS

## **Solid State Thermodynamics: Knudsen Cell Mass Spectrometry and High-Temperature X-Ray Diffraction**

Hugo F. Franzen

*Department of Chemistry and Ames Laboratory-DOE,  
Iowa State University, Ames, Iowa 50011*

The study of the thermodynamics of vaporization reactions by high-temperature techniques has always been motivated in part by the realization that the nature of the reactants and products in such reactions cannot always be inferred from measurements made on quenched samples and at lower temperatures. This is true for the condensed phases as well as for the vapor species. In particular, the occurrence of solids with wide ranges of homogeneity can change the character of the net vaporization reactions. In order to determine the nature of such reactions, methods have been devised which provide information about partial and total pressures at temperature including Knudsen-effusion mass-spectrometric, torsion-effusion and mass-loss effusion. In our laboratory mass-loss and mass-spectrometric measurements are made simultaneously to provide a uniquely powerful tool for the study of incongruent, as well as congruent, vaporizations. The technique has the weaknesses of uncertainty in measured temperature, leading to uncertainty in calculated enthalpy changes, and uncertainty concerning the effects of diffusion during incongruent vaporization which are more than overcome by the strength of providing information about reaction processes and homogeneity ranges at temperature. These strengths and weaknesses will be discussed with particular reference to the transition-metal aluminide systems studied in our laboratory (Ta-Al, Zr-Al, Nb-Al, and Mo-Al).

The study of the thermodynamics of intermetallic systems at high temperatures can be significantly strengthened by the knowledge of structure changes with changing temperature. We have found that high-temperature diffractometry provides substantial insight into the phase behavior of intermetallic systems. Phase behavior in the Rh-Ti, Ru-Ta, Ru-Nb, Mn-Au and V-Ir systems, as determined by powder X-ray diffraction and Rietveld full-profile refinement, will be discussed. The relationship of such information to the interpretation of vaporization studies will be illustrated with the example of the Lu-S system, a system for which the combination of recent high-temperature diffraction results with information from prior vaporization measurements has led to the identification of a new nonstoichiometric  $\text{Lu}_2\text{S}_3$  phase.

## Thermodynamics of Pd-As Alloys

H. Ipser, R. Krachler, and K.L. Komarek

Institut für Anorganische Chemie, Universität Wien,  
Währingerstr. 42, A-1090 Wien, Austria

A knowledge of the ternary Pd-Ga-As phase diagram is essential to an understanding of the reactions between palladium and gallium arsenide in Pd/GaAs contacts. Different procedures have been developed in the past to calculate (estimate) ternary phase diagrams from the thermodynamic properties of the limiting binary systems. In the case of the Pd-Ga-As system any such attempt is severely hampered by the almost total lack of thermodynamic information on the binary Pd-As system. Thus it was the goal of the present work to determine thermodynamic properties of solid and liquid Pd-As alloys.

An isopiestic method was used to measure arsenic vapor pressures in the composition range from 30 to 67 at% As. Due to the very low vapor pressure values in the solid phases with  $x_{As} \leq 0.33$  most of the data points were situated in the liquid in the temperature range between 600 and 1000°C, with a small number of points at lower temperatures in solid PdAs<sub>2</sub>.

The evaluation of these isopiestic measurements was made difficult by the fact that the values for the equilibrium constant of the reaction



differ widely throughout the literature. With the assumption that in the temperature range of our experiments arsenic vapor consists of As<sub>4</sub>-molecules only (as suggested by the data in Hultgren et al. (1)) a noticeable temperature dependence of the partial molar enthalpies of arsenic was obtained which would be rather unusual. Therefore equilibrium constants reported by Murray et al. (2) were used to calculate the thermodynamic activities of arsenic, and from their temperature dependence partial molar enthalpies were derived. From the measurements it could also be shown that PdAs<sub>2</sub> has a very narrow homogeneity range, i.e. it is essentially a line compound.

(1) R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, and D.D. Wagman, Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, OH (1973), 39.

(2) J.J. Murray, C. Pupp, and R.F. Pottier, J. Chem. Phys. 58 (1973), 2569.

# Simple Forms of the Gibbs-Duhem Integration for $k$ -gaseous Multicomponent Systems

Zhi-Chang Wang, Reinhard Lück and Bruno Predel

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft  
and Institut für Metallkunde der Universität Stuttgart,  
Seestrasse 75, D-7000 Stuttgart 1, BRD

Nagamori and Yazawa<sup>1</sup> first presented an integration of the Gibbs-Duhem equation for di-gaseous quaternary systems in 1988 dealing with the calculation of unknown activities of two components from known activities of other two components. As pointed out by themselves,<sup>1</sup> however, their formulae are very complex.

In this paper, three alternative forms of the Gibbs-Duhem integration have been presented for the di-gaseous quaternary systems and extended to  $k$ -gaseous  $(k + 2)$ -component systems (here  $k$  refers to any natural number), for both of which only one set of differentiation and one set of integration is required for the homogeneous phase and the differentiation can further be saved when one of them is applied to multiphases. Finally, the results have also been extended to  $k$ -gaseous  $c$ -component systems with  $c \geq k + 2$ .

## Reference

1. M. Nagamori and A. Yazawa, *Trans. JIM*, 1988, **29**, 798.

## PHASE EQUILIBRIA IN $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ SUPERCONDUCTORS

Th. Hehenkamp and F. Faupel

Institut für Metallphysik der Universität Göttingen,  
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In order to measure the decomposition of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (1, 2, 3) high- $T_c$ -superconductors a DTA apparatus was specially designed. It should provide sufficient sensitivity to detect even small thermal events like oxygen desorption or the tetragonal-orthorhombic phase transition and be resistant to oxygen. The instrument can measure under a pressure controlled atmosphere up to  $1200^\circ\text{C}$  and at heating (cooling) rates as low as  $0.1\text{ K/min}$ . The pressure control via PC permits either to maintain oxygen pressure or oxygen activity constant.

The thermal decomposition of 123 takes place at  $1024^\circ\text{C}$  and 1 bar oxygen pressure. It is pressure dependent at a rate of approximately  $30^\circ\text{C}$  per decade in oxygen pressure between 1 bar and 10 mbar. At the decomposition temperature the specimen melts partially and is reacting back to 123 upon cooling not completely. Thermal events are observed at different and sometimes much lower temperatures indicating that the reaction does not go to completion upon cooling. The different phases observed in the mixture are identified by x-ray diffraction and quantitative electron-probe-microanalysis of all elements. The phase distribution is again dependent on oxygen pressure. The results are compared with current data of the literature.

This work is being supported by BMFT under grant No. 13N5495.

# **OXYGEN PARTIAL PRESSURE OF Y-Ba-Cu-O FROM DIRECT MEASUREMENTS**

**F. Faupel and Th. Hehenkamp**

**Institut für Metallphysik der Universität Göttingen,  
Hospitalstr. 3-5, D 3400 Göttingen, F. R. Germany \***

Powder samples of Y-Ba-Cu-O were characterized by differential thermal analysis, x-ray diffraction, resistivity and magnetic measurements. The total equilibrium pressure was measured directly by means of a piezo-resistive pressure gauge as function of temperature. Mass spectrometry was employed to detect impurities in the gas phase. Substantial amounts of H<sub>2</sub>O and traces of CO<sub>2</sub> and N<sub>2</sub> were found in most samples. The onset temperatures of gas evolution were determined. The measurements of oxygen equilibrium pressure were carried out under conditions of minimized free volume and at different volumes. In the former case equilibration involves only minimal changes in composition and consequently no major diffusion of oxygen. Very short equilibration times were observed in this case. At high temperatures and pressures the results obtained from the direct measurements agree well with those deduced from isobaric measurements. At low temperatures and pressures the latter yield much lower values. The discrepancies will be discussed in terms of equilibration problems for the isobaric approach at low temperatures and pressures.

\* This work has been supported by BMFT under grant No. 13N5493.

## NEW AND OLD TOOLS IN MARTENSITIC TRANSFORMATION STUDIES

A. Amengual, V. Torra, A. Isalgue, F. Marco

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Dep. Fisica Universitat Illes Balears, 07071 Palma Mallorca

We have developed a system that allows the accurate control and programming of the temperature within a working space to study transformation cycles in shape memory alloys. The temperature detection is done by means of a Pt-100 resistance with a resolution of 0.001 Ohm (0.003 K). In our experimental set-up, with a sample of 1 g in mass, it enables us to work cycling with a resolution and reproducibility about 0.005 K. The maximum amplitude used is near 70 K. For intervals of 2 K, the minimum period lies around 200 s and for intervals of 50 K, about 1500 s. The Peltier effect is used for heating and cooling. It is excited by a current provided by a computer controlled power source. The system has been built in a very simple way and the working domain lies around the room temperature.

This controlled system has been applied to the study of the evolution of the martensitic transformation. With this goal, one needs to acquire one or more simultaneous measurements on a given sample. The available measurements are:

- a) Acoustic emission (A.E.) ring-down counting (MCS) or its classification by pulse high amplitude (PHA). In both cases a multichannel analyzer is used.
- b) Optical microscopy observation (until 700x) and simultaneous video recording for further study (260-360 K). The resolution of the optical microscope (1  $\mu$ m) allows the tracking of the small dimension changes during the growth of the martensite plates.
- c) Resistance changes. In this case, the use of techniques like the lock-in method allows to obtain a resolution near 0.1 % for resistance values of 1 milliOhm. This places the resistance measurement near the resolution available with calorimetry and acoustic emission. Therefore, it could be used in the study of the elementary transformation of burst-like behaviour.
- d) Unconventional DSC (223-353 K). With suitable signal processing, it gives a resolution near 1  $\mu$ V equivalent to 3  $\mu$ W. It can afford the energetic changes associated to the thermal cycles when austenite and martensite coexist.

Very important results are obtained from this experimental set-up, concerning:

- 1) Linking acoustic emission and unpinning processes.
- 2) Multi-interface effects in resistance measurements (dependence of the resistance on both mass and number of interfaces)
- 3) Entropy production in cyclic processes.
- 4) Time scales: Transformation temperature  $M_s$  vs. time as a function of dislocations concentration. Stabilization and ageing time scales.

## Gibbs Energy Determinations by Chemical Equilibria

H. Brodowsky

Institute for Physical Chemistry, University of Kiel, FRG

The application of the law of mass action was one of the earliest methods to obtain activity data in high temperature alloys and salt mixtures. It was, and still is, an important aspect in explaining and predicting metallurgical processes. It is also a welcome alternative for vapor pressure or emf measurements, as a check on other results or, in some cases, as the best available method.

Results are shown on the solubility of B and C in binary and ternary alloys, on Gibbs energies of Li, Al and Zr in Pt and Pd and on activity coefficients in binary salt mixtures. The equilibration was carried out in heterogeneous reactions with such gas mixtures as  $H_2-H_2O$ ,  $CO-CO_2$  or  $HCl-HBr$ .

## THERMODYNAMIC PROPERTIES OF THE AG - SB - ZN SYSTEM

Adolf MIKULA

Institut für Anorganische Chemie, Universität Wien,  
A-1040 Vienna, Währingerstrasse 42, Austria

The activity of zinc of several ternary Ag - Sb - Zn alloys was determined in the ternary Ag - Sb - Zn system at three cross sections with a constant Ag to Sb ratio of 3:1, 1:1 and 1:2 using an emf method. The measurements were carried out in the temperature range from the liquidus temperature up to 1123 K. The eutectic mixture of KCl - LiCl was used as an electrolyte.

From the activity data other thermodynamic properties were calculated. The Gibbs Duhem equation, in a treatment developed by Denken, was used to determine the integral Gibbs Free energy of the ternary system.

# **EXPERIMENTAL ENTHALPIES OF FORMATION OF SOME SOLID PHASES IN THE SYSTEMS PtTi and PtZr**

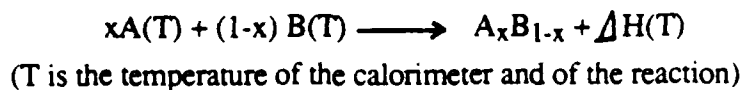
N. SELHAOUI, J.C. GACHON

Laboratoire de Thermodynamique Métallurgique, URA CNRS 1108,  
Campus Victor Grignard, Faculté des Sciences de l'Université de Nancy I,  
BP 239, F 54506 VANDOEUVRE LES NANCY CEDEX

The enthalpies of formation of Pt<sub>3</sub>Ti, PtTi, and Pt Ti<sub>3</sub> as well as those of Pt<sub>3</sub>Zr and PtZr<sub>2</sub> have been determined by our method of direct reaction calorimetry at high temperatures. The results are :

	Temperature/K	Enthalpy of reaction/J	Standard deviation/J
Pt <sub>0.75</sub> Ti <sub>0.25</sub>	1673	-94000	4300
Pt <sub>0.50</sub> Ti <sub>0.50</sub>	1673	-77100	3100
Pt <sub>0.25</sub> Ti <sub>0.75</sub>	1473	-59000	900
Pt <sub>0.75</sub> Zr <sub>0.25</sub>	1673	-106000	3400
Pt <sub>0.33</sub> Zr <sub>0.67</sub>	1500	-84000	3500

The enthalpies which are given correspond to the reaction :



A discussion will be presented to compare our results to former values, both experimental and computed using models, and to ascertain our accuracy of determination.

## THERMODYNAMIC INVESTIGATION OF THE SYSTEM Ag - Nb - Te

A. Brunner, H. P. Fritzer, and W. Sitte

*Institut für Physikalische und Theoretische Chemie*

*Technische Universität Graz, Graz, Austria*

The aim of this project was the investigation of the ternary system silver-niobium-tellurium by the use of solid silver ionic conductors in specially constructed solid state galvanic cells. The "galvanostatic intermittent titration technique" (GITT) applied to solid state materials is a very powerful method to obtain information on both phase relationships and thermodynamic data. Several silver ionic conductors ( $\text{RbAg}_4\text{I}_5$ ,  $\text{AgI}$  and  $\text{Ag-B''-Al}_2\text{O}_3$ ) were successfully applied for coulometric titrations between 25 and 500 °C. The working electrodes in the galvanic cell

$\text{Pt} / \text{Ag} / \text{Ag}^+\text{-conductor} / \text{Ag}_x\text{Nb}_y\text{Te}_z / \text{Pt}$

consist of binary or ternary starting materials. These have been prepared from the elements by solid state reactions in evacuated silica tubes or (in case of the niobium tellurides) grown as single crystals by chemical vapour transport. The binary system Ag-Nb shows no alloy formation and only a very slight mutual solubility at high temperatures, whereas in the binary system Nb-Te several niobium tellurides exist, which have been investigated by a number of groups (especially regarding the structural but less the thermodynamic properties). The third binary system Ag-Te has been investigated in detail by our group. No ternary compound could be found (as e.g. the proposed compound " $\text{Ag}_2\text{NbTe}_3$ ") in the investigated temperature range. Another question was the possible intercalation of niobium tellurides with silver as the niobium tellurides show interesting structures of low dimensionality. The experimental setup and the results with respect to the phase diagram and the thermodynamic properties are presented as far as possible between 25 and 500 °C. Furthermore, the advantages and limitations of this method are discussed.

THERMODYNAMIC STUDY OF Au-Pb-Pd TERNARY ALLOYS  
BY E.M.F MEASUREMENTS

S. SPAS .J. RIOU, J.M. MIANE. R. BARET

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and J.P. BROS.

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Université de Provence, 3 Pl V.Hugo,  
13331 Marseille Cedex 3, France.

In the course of the thermodynamic study carried out by our laboratory, concerning the alloys made of gold, lead, and an other metal, we have measured by potentiometry, the lead activity in a number of gold-lead-palladium liquid alloys over a large temperature range..

The thermodynamic functions and the phase diagram of this system have not been previously studied.

An electrode potential study of the liquid Au-Pb-Pd system has been conducted with the cell:  $\text{Pb} / \text{Pb}^{2+}$  in  $\text{LiCl} + \text{KCl}$  / Au-Pb-Pd in the temperature range 623 K- 1123 K.

Lead partial mixing functions were determined for 20 alloys. These measurements allow us to give the surface corresponding to lead partial free energy at 1123 K and a part of the liquidus surface of this system.

# **ELECTROCHEMICAL STUDIES WITH COMPOSITE ELECTROLYTES**

**C.B. Alcock  
Freimann Chair Professor  
University of Notre Dame  
Notre Dame, IN 46556**

## **ABSTRACT**

Following the review of solid electrolyte studies presented by Prof. Pratt at the Vienna meeting, the present state of the art on simple galvanic systems is briefly reviewed. It can be seen that there are a number of shortcomings in the technique, and a new technique involving a composite of solid electrolyte with a sensor dispersed phase which enlarges the scope of the method is presented. Examples are drawn from studies with stable oxides, sulphides, carbides and hydrides.

# Review of Alloys Modelling

Bo Sundman

With the aid of computers it is possible to obtain a very high degree of sophistication in the modelling of thermodynamic systems. One extreme is Monte-Carlo simulations of individual atoms in a lattice structure or gas. However, even today such models are limited to binary or ternary systems. With simpler models which only deal with average thermodynamic quantities like the enthalpy and entropy it is possible to obtain a good agreement with experimental information in multicomponent alloys. The drawback of a simpler model is that the simplifications may make the model less useful for predicting properties in regions with no experimental information. This means that it is important to base also simpler models on a reasonable physical picture of the nature.

Many new thermodynamic models have been proposed during the recent years and computers have made it possible to use even very complex models successfully. However, many models are very similar when they are carefully compared. The reason for this is that a model can only use a few independent variables i.e. the temperature, pressure, composition and internal degrees of freedom in a phase. Examples of internal degrees of freedom are species in a gas phase, associates in a liquid phase or different site occupancy in the sublattice model.

Models with no internal degrees of freedom are for example the many variants of the regular solution model with different type of extensions or excess terms like Redlich-Kister polynomials and ternary composition dependent terms. All these models assume an ideal entropy of mixing.

Modification of the entropy term give rise to models for ordering like the Bethe model or the Cluster variation method (CVM). In these models the fraction of bonds or clusters are used create internal degrees of freedom in a similar way as species in a gas. Introducing sublattices in order to describe interstitial solutions, intermetallic compounds or carbides will also modify the entropy term although the sublattice model assume random mixing on each sublattice. These models can also be augmented with excess terms like in the regular solution model.

The most complex phase to model is the liquid phase because it has such a wide range of properties. It is an inspiring work to attempt to develop a model applicable not only to liquid alloys but also slags, molten salts and aqueous solutions.

## THE METASTABLE PHASE IN Fe-C ALLOYS

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In the course of investigations of the phase transformations in Fe-C alloys by the Thermal Magnetic Analysis Method (in which the magnetic susceptibility of a dia- or paramagnetic substance is measured as a function of temperature) it was established that the melts of Fe-C alloys with contents of C up to 1.5 wt pct is crystallized into metastable bcc  $\delta$ -phase, in spite of stability of fcc  $\gamma$ -phase at high temperature at alloys with contents of C more than 0.51 wt pct [1,2]. This metastable  $\delta$ -phase is transformed into stable  $\gamma$ -phase after 50-100 C supercooling.

It was established also that melt of pure Fe is crystallised in any event into bcc  $\delta$ -phase even then the supercooling of melt was bellow than 1400 C, i.e. in the region of existence of fcc  $\gamma$ -phase [3]. This is the evidence of preference bcc structure at high temperature. The solidification into a intermediate phases was discovered in some fcc metals (Ni, Co, Cu, Pt) [2,4,5].

The obtained results can be explained by the assumption that solidification occur in accordance with the diagram of metastable equilibrium (if the lines of solidus and liquidus of  $\delta$ -phase is continued in the region of carbon content more than 0.51 wt pct ) [1].

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EXPERIMENTAL DETERMINATION OF THERMODYNAMIC ACTIVITIES OF  
METALS IN STRUCTURAL ALLOYS

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A B S T R A C T

The conventional electromotive force method facilitates the measurement of thermodynamic activity of the most electropositive component of an alloy. Techniques such as the Knudsen effusion, make possible the measurement of activities of at the most two metallic components at sufficiently high temperatures when their vapour pressures become detectable. However the metastable emf method recently developed by the present authors has permitted the direct measurement of activities of major metallic components in the austenitic phase of the AISI type 304, 316 and 316 LN stainless steels. The metallic activities in such steels are needed for an assessment of compatibility of these structural alloys with fuel and fission products on one hand and liquid metal coolants on the other in their service temperature range in fast nuclear reactors. This method could be extended to the characterization of the austenitic phase in a synthetic D-9 alloy, which is a candidate structural material for the future nuclear reactors including Integrated Fast Reactors (IFRs). The activities of metals in the AISI 300 series austenitic alloys have been made use of in the computation of threshold oxygen levels required for the formation of corrosion products on the structural alloys in contact with liquid sodium. The activities have also been used to compute the standard Gibbs' energy of formation of the complex  $M_{23}C_6$  phase in these alloys. A comparison of stabilities of  $M_{23}C_6$  in 304 and 316 stainless steels has shown that 304 variety is superior with respect to sensitization at temperatures above 900 K whereas at lower temperatures 316 is superior. This deduction from the Gibbs' energy consideration is substantiated by a cross over in the TTS diagrams of the two steels. Further, a comparison of these steels with D-9 alloy has been made with a view to assessing their tendencies to form intermetallic compounds with the metallic nuclear fuels clad by these alloys.

# THERMODYNAMICS OF THE Cu-Ti AND GaMgZn SYSTEMS AND METASTABLE PHASE FORMATION

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Current evaluations of the thermodynamic properties of the Cu-Ti system, while giving a reasonable fit to the phase diagram, do not predict the possibility of amorphization reaction by any technique. In fact, the free enthalpy curves for the liquid, extrapolated to low temperature to represent the glassy phase, never fall below those of competing solid solutions. This implies that the locus of points of equal free energy of the liquid and solid solutions ( $T_0$  curves) stands well above the glass transition temperature. Under these circumstances, rapid solidification would never produce a glassy alloy, because partitionless crystallization would occur at all compositions. On the contrary, amorphous Cu-Ti alloys are obtained in a wide composition range by rapid quenching, as well as solid state reactions.

We make the hypothesis that ordering takes place in the liquid phase on cooling from high temperature, finally leading to glass formation. This occurs at compositions where the excess specific heat of mixing is substantial. Therefore, we derive a new free enthalpy curve for the liquid accounting for an excess term due to ordering.

An estimation of an effective excess specific heat has been obtained at a few compositions from the difference between the heat of fusion and the heat of crystallization of melt spun ribbons in the temperature range of interest. The excess specific heat is considered to drop at the ideal (Kauzmann) glass transition temperature which is calculated from a suitable entropy cycle, using various descriptions of the entropy of the liquid.

$T_0$  curves for the terminal solid solutions have been computed which agree with the equilibrium phase diagram at high temperature, but open up a field for amorphization in undercooling conditions. The amorphizing range is compared with solid state reactions results.

The determination of the specific heat of a liquid GaMgZn alloy is under way in order to verify the presence of possible ordering also in a system from which quasicrystals nucleates easily. First results point towards the existence of an appreciable specific heat difference between liquid and crystal phases.

# THERMODYNAMIC CRITERIA OF GLASS FORMATION IN THE AS-SB-SE SYSTEM

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Glasses of the  $\text{As}_2\text{Se}_3$ - $\text{Sb}_2\text{Se}_3$ -Se system have applications as photoconductive sensors and, in general, as semiconductor materials. As a part of our general work on the study of the mechanisms responsible for glass-forming ability and thermal stability of some chalcogenide melts, we report here on the Gibbs free energy difference between the liquid and the crystalline phases at temperatures below the liquidus temperature as a measure of the driving force for eutectic crystallization. We also report on the Gibbs free energy of an alloy of any composition within the ternary system by taking into account the heat capacity difference between the liquid and the crystalline element or compound. For the solid phase we assume that there is no miscibility between Se,  $\text{As}_2\text{Se}_3$  and  $\text{Sb}_2\text{Se}_3$ . For the liquid phase we assume that it can be treated as a strongly associated regular (SAR) solution<sup>1</sup>. The results obtained are correlated with the known glass forming region in the system.

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**CVM and its applications to the thermodynamics of alloys**

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THREE DIMENSIONAL COMPUTER GRAPHICS  
FOR THE REPRESENTATION OF PHASE EQUILIBRIA  
IN THE QUATERNARY SYSTEM  $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$

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In spite of the relevance of the chemical system  $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$  (CAMS) to geoscientists and materials scientists alike, studies of microstructural (textural) development within this system are largely incomplete. Such studies have been hampered by incomplete and/or contradictory information regarding phase relations in the system CAMS and further complicated by the unwieldiness of graphical displays of four-component phase equilibria.

In order to address such difficulties, a technique for the graphical representation of phase equilibria in three- and four-component systems, utilizing commercially available solid modeling and computer graphics software, has been developed and proved helpful in assembling three-dimensional quaternary isothermal, isobaric diagrams from published information regarding phase equilibria within the system CAMS (including information from binary and ternary subsystems). Additionally, the graphical technique clearly reveals any inconsistencies between various data sources. Finally, the solid-modeling, graphical and computational capabilities made available by this technique can be used to provide real time rotation of three-dimensional diagrams, planar sections through three-dimensional diagrams, projections of quaternary phase equilibria over relevant temperature ranges into the composition tetrahedron, "lever rule" calculations, and determination of approximate crystallization paths. Thus the technique developed in this study for computer representation of phase equilibria overcomes much of the difficulty traditionally associated with information extraction from quaternary phase diagrams, providing a powerful tool to be used by researchers investigating phase transformations and morphological development in the system CAMS and quaternary systems in general.

# **A TIGHT-BINDING ANALYSIS OF THE COHESIVE PROPERTIES IN TRANSITION METAL CARBIDES.**

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The electronic structure and cohesive properties of transition metal carbides in NaCl structure are studied on the basis of a tight-binding recursion method. The electronic structure is analyzed in terms of a p-d interaction between the p orbitals of C and the d orbitals of the transition metal. A good agreement is found with the most sophisticated calculations like the ones based on the APW method. Concerning the cohesive properties of these compounds we have calculated the heats of formation of (Ti, Zr, Hf, V, Nb, Ta) C and compared with the experimental values. We are able to interpret the evolution of the experimental values when we go through a column or a row in Mendeleiev's table. At the end, the stability of the NaCl structure is compared with other non stoichiometric super structures.

# A Solution Model for the Relation between Enthalpy of Mixing and Excess Entropy in Liquid Binary Alloys.

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A thermodynamic solution model for liquid binary alloys has been derived on the basis of the configuration and vibration of atoms in alloys from the free volume theory. This model can explain the relationship between partial enthalpy of mixing  $\Delta\bar{H}_B$  and partial excess entropy  $\Delta\bar{S}_B^{\text{Ex}}$  of solute elements in infinite dilution in liquid binary alloys. The calculated results for the partial excess Gibbs energy of solute elements using the derived equation with the partial enthalpy of mixing obtained by Miedema's semi-empirical method<sup>1)</sup> are found to be in good agreement with the experimental values. Further, the following approximate relation has been derived :

$$\Delta\bar{H}_B \div \{14.0 / (1/T_{m,A} + 1/T_{m,B})\} \Delta\bar{S}_B^{\text{Ex}}$$

The above relation shows that the relation between  $\Delta\bar{H}_B$  and  $\Delta\bar{S}_B^{\text{Ex}}$  depends on the melting points  $T_{m,A}$  and  $T_{m,B}$  of the components of the alloys and the ratio of  $\Delta\bar{H}_B$  to  $\Delta\bar{S}_B^{\text{Ex}}$  becomes larger when the alloy is composed of components with higher melting points, as shown in Figure 1.

1) A.R. Miedema et al.: Physica 100B (1980), p.1

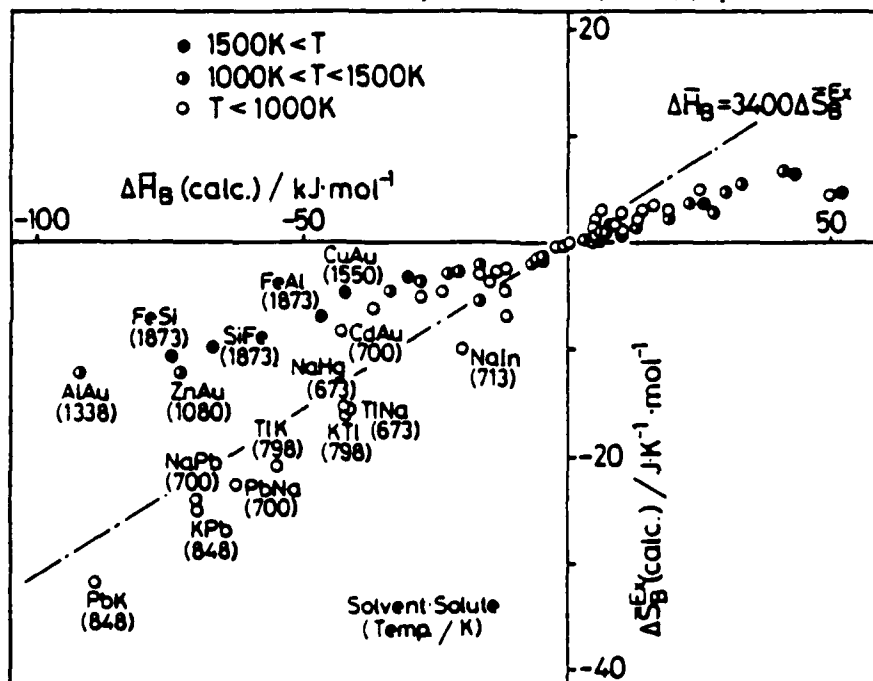


Figure 1

# Some relations between the enthalpy of mixing and deviations from free electron behavior observed in liquid ternary Cu-Ag-Ge alloys

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We have performed measurements of the Knightshift ( $K$  for Cu) in  $\text{Cu}_{(1-x)}\text{Ge}_x$  and  $(\text{Cu}_{50}\text{Ag}_{50})_{1-x}\text{Ge}_x$  alloys. They show significant deviation from free electron behavior around  $x=0.25$ . At about this concentration the Fermimomentum  $k_F$  and the first maximum in the structurefactor  $S(q)$  are related  $2k_F=q_{\text{peak}}$ ; this is supported by an analysis of conductivity data for Ag-Ge, Cu-Ge and  $\text{Cu}_{50}\text{Ag}_{50}$ -Ge using the  $t$ -matrix or Faber-Ziman formalism <sup>1</sup>. Within the framework of pseudopotential theory as used for the resistivity, an additional interaction is predicted which results in a minimum in the density of states. This should thus be most pronounced when  $2k_F$  and  $q_{\text{peak}}$  coincide <sup>2</sup>. By comparison with thermodynamic data <sup>3</sup> one finds

- i) the minima in  $K$  and  $\Delta H$  (enthalpy of mixing) occur at the same concentrations,
- ii) if the Cu/Ag ratio is changed the conductivity and Knight shift change little but the enthalpy of mixing disappears with increasing silver content.

The measurements suggest that a structure induced minimum in the density of states is present in all alloys. The thermodynamic properties on the other hand depend on details of the pseudopotential or band-structure parameter.

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# Rare Earth-Aluminium Alloys: Optimization of Thermodynamic Properties and Phase Diagrams of the La-Al and Ce-Al Systems

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The constitutional properties of the R-Al systems were recently assessed and presented by Gschneidner and Calderwood [1]. The following phases were reported for the La-Al and Ce-Al systems:

**La-Al:**  $\text{La}_3\text{Al}$  (peritectic),  $\text{LaAl}$  (peritectic),  $\text{LaAl}_2$  (congruent melting),  $\text{LaAl}_{2.4}$  (high temperature phase, peritectic),  $\text{LaAl}_3$  (peritectoidic),  $\alpha\text{-La}_3\text{Al}_{11}$  (low temperature phase),  $\beta\text{-La}_3\text{Al}_{11}$  (high temperature phase, congruent melting).

**Ce-Al:**  $\alpha\text{-Ce}_3\text{Al}$  (low temperature phase),  $\beta\text{-Ce}_3\text{Al}$  (high temperature phase, congruent melting),  $\text{CeAl}$  (peritectic),  $\text{CeAl}_2$  (congruent melting),  $\text{CeAl}_3$  (peritectoidic),  $\alpha\text{-Ce}_3\text{Al}_{11}$  (low temperature phase),  $\beta\text{-Ce}_3\text{Al}_{11}$  (high temperature phase peritectic).

As for the thermodynamics of the R-Al alloys several investigations are reported in literature [1]. In the specific case of the La-Al and Ce-Al systems the following thermodynamic properties are described:

**La-Al:**  $\Delta H_f$  of solid alloys (determined by liquid Al solution calorimetry by Colinet et al. [2] and Sommer et al. [3]),  $\Delta H_{\text{melt}}$  of several compounds (Sommer),  $\Delta \bar{G}_{\text{La}}$  at 800 K (e.m.f. measurements by Kober et al. [1]),  $\Delta H_{\text{mix}}$  of liquid alloys at 1200 K (Sommer). Aluminium activity of molten alloys at 1693 K (vapor pressure measurements by Kononenko [1]).

**Ce-Al:**  $\Delta H_f$  of solid alloys (determined by liquid Al solution calorimetry by Colinet et al. [2] and Sommer et al. [4], by direct calorimetry by Borzzone et al. [5]),  $\Delta H_{\text{melt}}$  of several compounds (Sommer),  $\Delta \bar{G}_{\text{Ce}}$  of solid alloys (e.m.f. measurements by Kober et al. [1]),  $\Delta H_{\text{mix}}$  of liquid alloys (by Esin et al.

[1] and Sommer [4]). Aluminium activity of molten alloys at 1673 K (vapor pressure measurements by Kononenko et al. [1]). Several contradictions appear between the different measured values. A similar situation was found by Ran et al. [6] while carrying out a thermodynamic optimization of the Al-Y system. To avoid these contradictions Ran et al. used the values estimated with the Miedema model for the  $\Delta H_f$  of the compounds. In our case however, if we consider only the calorimetric data obtained in refs. [2,3,4,5], there is very good agreement between them. Their plots moreover show trends, as a function of the composition, which generally agree with the phase diagram shapes. Using these data together with the phase diagram data the thermodynamic description of the systems was optimized. We used the procedure described by Lukas et al. [7]. The results obtained are briefly discussed and the computed values are compared with the experimental ones.

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## Determination of the thermodynamic properties of formation of alloys at high temperature.

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In this lecture we first analyse the various strategies used to obtain quantitative informations for the thermodynamic properties of formation of alloys : why to measure them , how to obtain them ?

In any case we are concerned with the Gibbs function of formation which can be separated into its two enthalpy and entropy contributions. The entropy is always very difficult to measure directly even if we consider the Nernst postulate. There exist two different types of derivation of the chemical potential versus temperature. The Van T'Hoff derivation give the partial enthalpy, whereas the Helmholtz derivation give the partial entropy. For this reason all the equilibrium methods, like mass spectrometry, E.M.F., effusion, isopiestic...are self consistent to determine simultaneously the enthalpy and entropy partial contributions. Nevertheless, when considering the rough accuracy of the derivations versus temperature, or versus inverse of temperature, it appears that calorimetric methods remain the most efficient ones to determine the enthalpies.

**Partial and integral enthalpies of mixing** can be measured directly in the cell of the calorimeter for **liquid alloys**. Very high temperatures impose appropriate devices and some of them, taken from literature, are presented in the lecture. For **solid solutions and compounds**, the **integral enthalpies of formation** are often measured. It is possible to use either indirect methods, like dissolution or combustion, or direct synthesis in the cell of the calorimeter. We are convinced that direct methods are the must, when possible, and we present the results obtained in our laboratory for the transition intermetallic compounds as an illustration of high temperature quantitative calorimetry. In the meantime, some other exemples taken in the literature prove that dissolution methods provide also accurate results when using the appropriate solvent. **Partial enthalpy of a compound in equilibrium with a liquid phase** can also be measured directly in the calorimeter.

Crossed strategies using simultaneously enthalpy and Gibbs-function measurements are very reliable to deduce the entropy contributions.

In years gone by, it was necessary to measure any partial quantity of a component in a binary alloy up to the nil-concentration to practice the Gibbs-Duhem integration. At the present time the optimization methods used for phases-diagram calculation, are able to take into consideration any thermodynamic information, even fragmentary, enthalpy or entropy one, partial or integral. Mixed together in the same modelization program, fragmentary pieces of information are able to provide a rather good estimation of the unknown data, and to give back a coherent set of thermodynamic data for all the concerned phases. The extension of these method to multicomponent systems is also possible. Considering the progress realised in such "calphad"-optimization, experimental laboratories have to include, in their set of tools, the calculation of the phase diagrams as a new "experimental technique". We illustrate this point of view on various exemples taken from our laboratory and from literature.

APPLICATION OF SOLUTION MODELS  
TO DIFFUSIVITY STUDIES IN MULTICOMPONENT ALLOYS

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The "diffusivity" of an n-component alloy is a property matrix that contains  $(n-1)^2$  diffusion coefficients. Variation of the diffusivity with composition is important when modelling the kinetic behavior of high temperature alloys or when measuring kinetic properties of quaternary or higher order alloys. The three factors which influence this variation are the atomic mobilities, the Kirkendall effect, and the curvature of the free energy function. For "ideal solutions" the variation is caused by the Kirkendall effect alone and the free energy factor is not important. However, for "regular solutions" the free energy factor may either increase or decrease the variation depending on the interaction parameters. In this regard the interaction parameters affect the composition range over which the diffusivity can be approximated by constant diffusion coefficients.

## Establishing Phase Relationships by Means of the Temperature Gradient Diffusion Technique

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The sequence of diffusion layers in a binary diffusion couple reflects the sequence of phases in the corresponding phase diagram. If the diffusion processes are slow, the amount of energy required for boundary movement is small, and diffusion couples can then be an exceptionally suitable tool for investigating phase equilibria. By microanalytical concentration measurements across the layers direct information about the composition and homogeneity ranges of coexisting phases at a given temperature is available. A series of isothermal diffusion couples which are heat-treated at different temperatures can be used to construct the phase diagram.

In the present study the diffusion couple technique has been further developed by the introduction of a temperature gradient parallel to the diffusion layers. Through metallographic inspection of the diffusion couples together with EPMA measurements, a direct representation of a phase diagram in a temperature range given by the temperature gradient of the experiment could be achieved. This method also makes it possible to observe the temperature sequence of phase reactions within a very small temperature range where more conventional methods for the investigation of phase equilibria may not give conclusive results.

An application of this technique is presented for the Ti-N system, where several phases occur at concentrations from 28 - 33 at% N and in a relatively narrow temperature range. The phase equilibria in the Ti-N system could thus be established in the temperature region of 1000 - 1150°C, something not possible using arc-melted and heat-treated alloys.

## Enthalpy of Formation of $\text{Ni}_3\text{Al}$ with Ternary Additions

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In commercial nickel-base superalloys the elevated temperature strength is attributed to the presence of a dispersion of  $\text{Ni}_3\text{Al}(\gamma')$  in solid solution matrix. Additions of third elements in  $\text{Ni}_3\text{Al}$  can substitute exclusively Al or exclusively Ni or both sites. We have determined the enthalpy of formation of  $\gamma'$  phases (ternary additions: Mn, Si, Fe, Cr, Ga, Co and Cu) in their homogeneity range as a function of concentration of the third component using a high temperature solution calorimeter. The results will be discussed in relation to the site preference of the ternary additions.

## CALORIMETRIC STUDIES ON LIQUID Al-Li-Mg ALLOYS

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In the high temperature reaction calorimeter integral enthalpies of five series of liquid Al-Li-Mg alloys were measured. In first four series to starting bath  $\text{Mg}_{0.11}\text{Al}_{0.89}$ ,  $\text{Mg}_{0.25}\text{Al}_{0.75}$ ,  $\text{Mg}_{0.50}\text{Al}_{0.50}$ ,  $\text{Mg}_{0.75}\text{Al}_{0.25}$  (concentration in molar fractions) solid lithium, while in fifth series to  $\text{Mg}_{0.5}\text{Li}_{0.5}$  solid aluminium were added. In each series, measurements were repeated three times at constant temperature not exceeding  $700^{\circ}\text{C}$ . Main experimental difficulties were connected with corrosion of the containers (alumina or iron crucibles) and with creeping of alloys out of the crucible changing composition and destroying the Ni-NiCr thermopile situated below the reaction crucible. Calibration was performed by adding Mo, which has a known enthalpy content, between additions of the alloy components during the measurements.

Data within the same series were consistent within the order of  $\pm 1$  kJ/mol even when measured at slightly different temperatures. Results of integral enthalpies show reasonable agreement with values calculated on the basis of respective binaries except higher concentrations of the third component. The latter suggest probably the necessity of introducing in interpretation method of the ternary interaction term.

The measurements in each series were continued until evident tendency of precipitation was observed caused by additionally evolved heat when crossing of the equilibrium lines. This tendency does not agree with the liquidus surface of the calculated phase diagram by Saboungi et al. (Calphad, 1, 1977 pp. 237-251) on the basis of constituent binaries. Therefore it seems that the ternary Al-Li-Mg system require further experimental investigations not only by calorimetry but also by emf as well as of phase diagram by thermal analysis and separate studies on the ternary intermetallic compounds not taken into consideration in Saboungi's calculations.

# LIQUID ALLOYS WITH STRONG INTERACTIONS\*

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## Abstract

Liquid alkali metals alloyed with either Pb or Sn show remarkable features in the electrical, electronic, thermodynamic, and structural properties at the "octet" composition and/or the equiatomic composition. A review of these properties will be presented, with special emphasis on the complementarity of information obtained from different experimental results. Recent molecular dynamics simulations of the structure and atomic motions of the equiatomic alloys reveal interesting insights into the correlations of atomic triplets and explain results obtained from inelastic neutron scattering.

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†On leave from Solid State Physics Laboratory, University of Groningen, Groningen, The Netherlands.

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# **SOLUTE-SOLVENT DROP CALORIMETRY OF TRANSITION METAL INTERMETALLIC COMPOUNDS**

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The information which is available on the enthalpies of formation of transition metal intermetallic compounds leaves much to be desired. Since the early transition metals are very reactive, and most intermetallic compounds are quite refractory, it has proved difficult to study them by high-temperature liquid-metal solution calorimetry. The bulk of previously reported enthalpy data on intermetallic compounds were obtained either from solid + solid synthesis calorimetry or were derived indirectly from e.m.f. or vapor pressure measurement. In either case the data are associated with significant experimental uncertainties; also, it is difficult for the reader to assess the magnitude of the errors from published information. The authors have developed a new calorimetric method, "solute-solvent drop calorimetry", which has proved useful in the study of intermetallic and other refractory compounds.

This method involves the dropping of small capsules which contain a solid mixture of solute and solvent from room temperature into a high-temperature calorimeter, where they generate a homogeneous liquid mixture. The "solute" is either the refractory compound or a mechanical mixture of its constituent elements. In our studies of intermetallic compounds the "solvent" was usually a mixture of platinum or palladium with germanium. The development of this method will be outlined and its application to intermetallic compounds of Group IVA metals with platinum group metals will be reviewed.

## Thermodynamic Effects, Seen on the Atomic Sites, in Strongly Bound Liquid Alloys

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The strong bonding effects which are characteristic for many liquid alloys A-B between chemically dissimilar metals must be expected to be accompanied by considerable changes of the electronic states of the constituent atoms. Also, the interatomic dynamics are changed. The dependencies of these changes on temperature, on concentration or on the system considered, should reveal important information about the bonding mechanism and bonding strength in these liquid alloys. We discuss Knightshift data (new results on metal-Te, and literature data), which show that on either constituent A or B, localized electronic effects of the bonding can be observed, and that they develop rather asymmetrically for A and B (cases are Sn-Te, Cu/Ag-Te; Au-Cs etc.). These effects can be well understood within a model of a chemical reaction  $A+B \rightarrow AB$ , where the hyperfine interaction selects the atom (A or B) and then differentiates between left hand and right hand side states (A,B vs. AB). Similarly, effects of bonding on dynamics can be seen in nuclear spin relaxation (Ott et al. Progr. NMR Spectroscopy 21 (89) 203). Using additional data (electric and magnetic field fluctuations) it appears possible to derive the bonding character (metallic/ionic/covalent) in liquid alloys.

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## Disorder-Order Transition Kinetics in L1<sub>2</sub> type Alloys

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The study of kinetics of ordering in L1<sub>2</sub>-type alloys disordered by quenching is feasible when the critical temperature is below the melting temperature but above room temperature. Diffraction experiments can trace the ordering through the appearance of superlattice peaks and calorimetric measurements can provide the ordering energy which is a measure of the stability of the L1<sub>2</sub> superlattice.

While calorimetric studies of the ordering transition in some L1<sub>2</sub> type alloys have been studied by K. Mitsui et al (1), such studies on Ni<sub>3</sub>Al-Fe alloys have only been reported recently using the disordered state obtained by rapid quenching from the liquid state (2). This paper reports on first results extending the work of K. Mitsui to high vacancy supersaturation conditions obtained by rapid quenching.

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SHORT-RANGE ORDER-DISORDER TRANSITION IN LIQUID ALLOYS  
ACCORDING TO THE ASSOCIATED MODEL.

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In these two last decades, many careful investigations on liquid alloys showed that in many cases their thermodynamic behaviours are very sensitive to temperature. We pointed out as early as 1969 /1/ that compound-forming tendency of melts with negative deviations to ideality is the rule rather than the exception. These melts have strong negative values of the enthalpy of formation, positive excess  $C_p$  of formation and their entropy of formation often shows a minimum with respect to composition. Application of the regular associated model to this class of binary alloys shows that such a behaviour can be attributed to the dependence on temperature of their chemical short-range order and allowed us to point out that these dependence takes place in a more or less narrow temperature range according to the value of the standard parameters of formation of the associates /2/. In some cases the thermal evolution can be assimilated to a genuine second order transition.

In order to clarify the problem we will describe in this paper the behaviour of ideal associated systems. We will state the following points :

- 1) Associated liquids do not become completely disordered. Still at high temperature there is some residual negative enthalpy of formation due to the persistence of unnegligible quantities of associates.
- 2) The more negative the standard entropy of formation of the associates the more restricted the temperature range where the transition occurs and the more important the transition enthalpy (defined as the difference between the enthalpy of formation at  $T=\infty$  and  $T=0$ ).

As an experimental example we will show the results obtained in the Te-rich Ge-Te eutectic where such a transition takes place /3/.

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## GLASS FORMING ABILITY IN CHALCOGEN RICH Se-Te-Ge GLASSES

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The glass forming ability (GFA) of alloys produced by the application of rapid solidification from the melt has been discussed extensively from various viewpoints. It appears to be established that only a limited range of multicomponent systems may be solidified into an amorphous glassy state by the rapid solidification technique. Among them, those that can be solidified into a glassy phase at rather low cooling rates include the chalcogenide alloys.

The aim of this work is to look into the GFA of pure Se-Te alloys compared to that obtained with some small additions of Ge on them. The empirical parametrization of the GFA is obtained from the crystallization kinetic results. The thermodynamical approach is used to calculate the Gibbs free energy of formation of each alloy. The results of the calculation give qualitative agreement with the experimental results.

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STRUCTURAL AND THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS AT THE EUTECTIC COMPOSITION : CASE OF  
THE GOLD-SILICON AND GERMANIUM-TELLURIUM SYSTEMS .

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In a review paper (1), the importance of the relative heat capacity of a liquid alloy has been emphasized and presented as a sensitive indicator of the chemical short-range order (CSRO). The word "chemical" is usually associated to distinguish the ordering (here tendency for heterocoordination) from the topological effects . Obviously, the diffraction experiments which yield the liquid structure factor  $S(q)$  related by Fourier transform to  $g(r)$  which describes the probability for two atoms to be at a distance  $r$  are very attractive for this purpose.

The aim of this study is to bring together the experimental informations obtained from both methods of investigation.

Two different systems have been selected, the gold-silicon and the germanium-tellurium systems for the following reasons:

- both phase diagrams present an eutectic (  $x(\text{Au})=0.81$  in the first case and  $x(\text{Te})=0.85$  in the second one ) where the probability for CSRO to take place is important.
- both systems have been investigated by calorimetry in the laboratory in order to obtain the relative heat capacity in a large temperature range :  $T_{\text{eut}} + 600$  in the Au-Si alloys and  $T_{\text{eut}} + 300$  in the Ge-Te alloys .

The neutron diffraction measurements have been performed at I.L.L. on the diffractometers D20 and D48 ; the following preliminary observations can be made on the total structure factors : for Au-Si, the total structure factor shows the behaviour of a liquid metal with no observed variation versus the temperature ; for Ge-Te, the total structure factor shows three main peaks with quite the same height, presenting a remarkable evolution when increasing temperature .

The corresponding maximum values of the relative heat capacities are 18.8 and 180  $\text{JK}^{-1}\text{mole}^{-1}$  (resp. for Au-Si and Ge-Te).

REFERENCE

RELATIVE SOLID SOLUBILITY IN BINARY ALLOYS  
OF TRANSITION METALS

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Predictions of relative solid solubility in binary alloys of transition metals are made using the semiempirical theory of Miedema [1]. In this treatment the heat of solution of a solute metal S in a matrix metal M includes a chemical contribution, an atomic size mismatch contribution and a structural contribution. For low temperature phases, for which the necessary elastic moduli of transition metals are well known, the model's predictions are in good agreement with the available experimental information. We also calculate relative solid solubilities in some high temperature phases containing Zr and Hf, whose shear moduli are expected to be much smaller in this region than at low temperatures. Although these latter calculations are only approximate, because the exact temperature dependence of the elastic moduli of the various metals involved are not well known, the model's predictions are also encouraging in this case.

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Work supported by DGICYT of Spain (Grant PB86-0654-C02).

# THE INFLUENCE OF CRYSTALLINE ORIENTATION OF Cu-Zn-Al SHAPE MEMORY SINGLE CRYSTALS IN THERMAL EFFICIENCY.

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The thermal efficiency on three single crystals of identical chemical composition (68.67%Cu, 16.22%Zn and 15.11%Al in atomic percentage) with an electron to atom ratio of 1.464 and different crystalline orientation (311), (321) and (322) has been determined.

Due to the shape memory effect, these single crystals can convert heat produced by temperature gradient into mechanical energy. The thermal efficiency is given by the equation:

$$\eta_t = \frac{\Delta H \Delta T_0}{T_0 [C_p \Delta T_0 + \Delta H(\sigma)]}$$

where:

$C_p$ : specific heat of alloy.  $\Delta H$ : ( $\beta \rightarrow$  Martensite) transformation enthalpy, being  $T_0$  the equilibrium temperature.

$\Delta H(\sigma)$ : ( $\beta \rightarrow$  Stress Induced Martensite, S.I.M.) transformation enthalpy, can be expressed as:

$$\Delta H(\sigma) = \frac{\Delta H \cdot T_0(\sigma)}{T_0}$$

being  $T_0(\sigma)$  the equilibrium ( $\beta \rightarrow$  S.I.M.) transformation temperature.

The calorimetric system allows the measurement of the characteristic temperatures, as transformation enthalpy calculated by integration of calorimetric curve. The compression tests were carried out on the same samples, after calorimetric test, using Hounsfield W machine at different temperatures (0, 10, 20, 30, 50 and 70°C).

Thermal efficiency calculated, shows that there is a strong influence with the crystalline orientation of the single crystals.

Crystalline orientation	$\eta_t$ (%)
(311)	1.06
(321)	1.50
(322)	2.03

Thermal efficiency is greater when the interplane distances are small. When the interplane distances are small, the martensitic plates have a greater amount of stored elastic energy, since in this case there is more internal stress and there are contact surfaces between martensite plates and  $\beta$ -interphases. This brings about a greater conversion to mechanical energy with the same calorific energy.

## Application of the Wagner-Schottky Model to Nonstoichiometric Intermetallic Phases

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The Wagner-Schottky model (1) is a statistical model for crystalline ordered nonstoichiometric phases. Nonstoichiometry is caused by statistically distributed point defects in the ordered crystal lattice. Thermal agitation causes the existence of additional point defects. Using the concentrations of the different defects at stoichiometry (which are entirely due to thermal agitation) as parameters it is possible to calculate their concentrations at any composition within the phase boundaries.

In the non-equilibrium case the Gibbs free energy  $G$  of one mole of the substance in the interior of the crystal is a function of the various point defect concentrations  $v_1$  to  $v_n$ .

$$G = G(v_1, \dots, v_n)$$

The equilibrium condition for constant mole numbers  $N_1$  and  $N_2$  (in the case of a binary phase) and constant temperature and pressure can be written in the following form:

$$(dG)_{p,T,N_1,N_2} = (\partial G / \partial v_1)_{\text{equ}} dv_1 + \dots + (\partial G / \partial v_n)_{\text{equ}} dv_n = 0$$

where the index "equ" means "equilibrium".

Because the mole numbers  $N_1$  and  $N_2$  are kept constant and because several possible transformation reactions exist between different species of point defects, one obtains exactly  $(n-1)$  additional equations so that the  $n$  unknowns  $v_1$  to  $v_n$  can be evaluated.

In some cases the distribution of the point defects is not statistical: the occurring superstructures in the crystal lattice can then be treated in the model by introduction of additional sublattices.

Using the Wagner-Schottky model in the above form the authors have treated the B2 and B8 structures in a more general way than previously.

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## Long Range Order Parameters for Multicomponent Compounds

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In the investigation of Heusler alloys and related intermetallic compounds a change of the long range order may be observed during thermal treatment. An ab initio description of the long range order of multicomponent alloys is carried out by a special matrix. This matrix is defined by the atomic fractions of each component for each sublattice. Vacancies can be treated as a separate component. The large number of parameters can be reduced to some extent taking into account the boundary conditions. These parameters would be basic for a multicomponent Bragg-Williams theory.

The processes of ordering and disordering will be described by the loci of composition in geometrical representations for the different sublattices. Continuous transitions as well as transformations in steps are possible.

MONTE CARLO SIMULATION OF COVALENT LIQUIDS USING A QUANTUM  
MECHANICAL DESCRIPTION OF THE ENERGY

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The crystalline structures of group-V, -VI, -VII elements show a systematic behaviour which can be explained by a p-bonding mechanism and a Peierls instability. Our present results concern group-V elements.

Diffraction experiments (1) have shown that in amorphous and liquid structures the Arsenic atoms have 3 first neighbours with interatomic distances nearly identical to crystalline As. The same holds true for Phosphorus. This supports the argument that the Peierls distortion is still present in non crystalline structures, and, indeed, a moment calculation of the electronic density of states has proved (2) that the periodicity is not a necessary condition for the Peierls instability.

A molecular dynamics simulation of liquid Arsenic, using effective pair interactions has already been performed (3) and yields a correct representation of the structure.

We report preliminary results of a Monte Carlo simulation of p-bonded liquids. The cohesive energy of the system is calculated using a tight-binding approximation and considering only  $pp\sigma$  interactions. The density of states is calculated at each Monte Carlo step using a continued fraction limited to the fourth moment : this means that the first and second neighbours of each atom are taken into account for the quantum mechanical calculation of the cohesive energy. The hopping integral  $\beta(r)$  and repulsive energy  $V(r)$  are assumed to behave like :

$$\beta(r) = \beta_0 \exp(-qr) \text{ and } V(r) = V_0 / r^p.$$

The pair correlation function for a group-V liquid (half filled p-band) clearly shows that the Peierls distortion is still present in the liquid state (3 first neighbours) at various reasonable temperatures.

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Enthalpy of formation and phase diagram  
of the Ga-Pb system

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Abstract :

With an high temperature CALVET calorimeter, using both the direct and indirect drop methods of mixing, the molar enthalpy of formation of liquid Ga-Pb alloys have been measured at 890 K on a large concentration range ( $x_{Pb} = 0.77$ ).

Several values of the mixing enthalpy of this binary system have been published; the shape for  $0 < x_{Pb} < 0.5$  and the maximum value agree with the values of KWONG /1/.

The only published equilibrium temperatures /2/ of this system, on the entire concentration range are in good agreement with ours D.T.A experiments and heat capacities measurements in the solid and liquid states using a D.S.C. calorimeter.

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